



# Efficient photocatalytic CO<sub>2</sub> reduction over Co(II) species modified CdS in aqueous solution

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## ABSTRACT

Efficient photocatalytic reduction of CO<sub>2</sub> into value-added chemical fuels has been a thorny, challenging and long-term project in the environmental/energy fields due to the low efficiency, especially in the inorganic aqueous environment. In this report, we present a facial approach to modify CdS with Co(II) species through controlling decarboxylation of the Co-EDTA precursor for improved CO<sub>2</sub> reduction. Performance evaluation and microstructure characterization reveal that the resulted tetra-coordinated Co(II) modified CdS exhibits the most optimized CO evolution rate of 9.8 μmol h<sup>-1</sup> (i.e., 392 μmol h<sup>-1</sup> g(catalyst)<sup>-1</sup> with TOF of 7.94 h<sup>-1</sup>) in aqueous solution under visible light, where the competitive hydrogen evolution reaction is significantly inhibited. Further investigation implies that the fully utilized Co(II) active sites, the tetra-coordinated Co(II) species, the favorable interaction between CO<sub>2</sub> and Co(II) sites and efficient charge transferring ensured the high efficiency and improved selectivity. This work would provide a good strategy for the structure engineering of catalytic site to improve photocatalytic CO<sub>2</sub> reduction.

## 1. Introduction

In the search trend to relieve the energy crisis and the increased panic from the climate change and sea levels-rising, photocatalytic CO<sub>2</sub> reduction has been considered as one of the most attractive routes to take advantage of the abundant solar energy and recycle CO<sub>2</sub> resource, mimicking the natural photosynthesis cycles for long-term CO<sub>2</sub> utilization [1–6]. To realize the ultimate goal, the challenging reductive half-reaction of CO<sub>2</sub> fixation needs to be well addressed, including increasing the efficiency and selectivity, especially minimizing the co-existed water reduction in the aqueous environment. Due to the chemical inert of linear CO<sub>2</sub>, one-electron reduction of CO<sub>2</sub> to CO<sub>2</sub><sup>-</sup> is highly unfavorable in thermodynamic with the standard potential of -1.9 V vs. NHE [7–9]. Although the proton assisted multi-electron reduction is substantially more favorable, suitable catalysts are still essential in the multi-proton and multi-electron reduction processes to decrease the kinetic resistance [10–16]. As reported by Ishitani and the coauthors, homogeneous system with Ru-based mononuclear or

multinuclear complexes exhibited prominent efficiency in the selective photocatalytic CO<sub>2</sub> reduction compared with the activity observed in heterogeneous system [17–19]. It is well-established that efficient electron transfer between the covalently linked photosensitizer and the catalytic sites, and the uniquely designed configuration of catalytic sites contribute to the outstanding performance [20–23]. More importantly, constructing homogeneously dispersed catalytic sites over semiconductor with selective and efficient catalytic activity would make up the gap between heterogeneous and homogeneous photocatalytic CO<sub>2</sub> reduction, with prospect of maintaining both high activity and long durability. Ru(II) complex was also successfully utilized as molecular catalyst combined with semiconductor for CO<sub>2</sub> reduction in the recent work by Ishitani [24,25]. However, the scarcity and high cost of Ru inspired the exploration for abundant transition metal-based alternative catalyst. To the best of our knowledge, structure engineering of transition metal catalyst anchored on semiconductor for selectively efficient CO<sub>2</sub> reduction in aqueous solution is still rare [17,26–32]. Since CdS has been widely used in visible-light photocatalysis with negative

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enough conduction band [33,34], herein, we first present a new strategy to anchor well-dispersed Co(II) species on CdS semiconductor support through controlling the decarboxylation of EDTA (ethylenediaminetetraacetic acid) ligand in the Co-EDTA precursors during different-temperature calcination under argon, which resulted in one kind of tetra-coordinated Co(II) species that exhibits high efficiency toward CO<sub>2</sub> reduction into CO in aqueous solution with Na<sub>2</sub>SO<sub>3</sub> as a sacrificial reductant under visible light irradiation, with a significantly inhibited hydrogen evolution rate.

## 2. Experimental section

### 2.1. Materials preparation

Ethylenediamine-*N,N,N',N'*-tetraacetic acid cobalt(II) disodium salt tetrahydrate (Co(II)-EDTA) was mixed with purchased CdS in different mole ratios (0.36%, 0.5%, 0.7%, 1.4%) in methanol solution by stirring at 60 °C for solvent evaporation. The default mole ratios of Co(II)-EDTA to CdS is 0.7%. The resulted mixture was calcinated at different temperatures (250, 275, 300, 350, 400 °C) under argon for 1 h and the obtained samples were referred to as CdS-CoE-*x*, in which *x* is the calcination temperature.

### 2.2. Characterization

Powder XRD was carried out on an X-ray diffractometer (Rint 2000, Altima III, Rigaku Co. Japan) with a Cu K $\alpha$  source. Thermogravimetric measurements were conducted on a Seiko Instrument thermogravimetry/differential thermal analyzer (TG-DTA 6200) under argon. Transmission electron microscopy (TEM) images, combined with energy dispersive X-ray spectroscopy (EDS) mapping were recorded with a field emission transmission electron microscope (JEM2100F, JEOL Co., Japan) operating at 200 kV. FT-IR spectra were recorded by Nicolet 4700 spectrometer with reflection mode. XPS measurement was carried out with electron spectrometer (PHI Quantera SXM, ULVAC-PHI Inc., Japan). The UV–vis absorption was measured with a UV–vis spectrophotometer (Shimadzu, UV-2600) using BaSO<sub>4</sub> as the reflectance standard reference. ESR measurements were carried out at room temperature on a JEOL JES-FA-200. PL spectra were recorded by a JASCO FP-6500 spectrofluorometer. The fluorescence decay curve was measured using a compact fluorescence lifetime spectrometer (QuantaTaurus-Tau, C11367), excited at 420 nm. EXAFS signals of the Co K-edge were recorded at 14 W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF, China) in the fluorescence mode for CdS-CoE-*x* samples and in the transmission mode for Metallic cobalt and cobalt sulfide. The electron beam energy was 3.5 GeV with the mean stored current was 300 mA. The energy of the X-ray was tuned using a fixed-exit double-crystal Si (111) monochromator. Metallic cobalt foil and cobalt sulfide were used for energy calibration and as references. The intensities of the incident and fluorescence X-ray were monitored by using standard N<sub>2</sub>-filled ion chamber and Ar-filled Lytle-type detector, respectively. Analysis of the obtained EXAFS data was performed using Athena and Artemis interfaces to the IFFEFIT software. All fits were performed in the R space with k-weight of 3.

### 2.3. Photocatalytic activity evaluation

Photocatalytic activities were evaluated by the CO<sub>2</sub> reduction from aqueous solution containing Na<sub>2</sub>CO<sub>3</sub> under visible light irradiation with sodium sulfite as electron donor. In detail, the 25 mg catalyst and 70 mL of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>3</sub> solution (0.3 mol/L and 0.06 mol/L) were added in a Pyrex glass reaction cell which was connected to a gas-closed system with a gas-circulated pump. Before the irradiation, the reaction cell was evacuated to remove the air completely. And then 80 kPa of pure CO<sub>2</sub> was inlet into the reaction cell. A 300 W xenon arc lamp with a UV-cut filter (to remove light with wavelength lower than 420 nm)

was used as light source. The produced CO was analyzed by an online gas chromatograph (GC-8A, Shimadzu Corp., Japan). The isotope test was carried out by using <sup>13</sup>CO<sub>2</sub> dissolved in NaOH as carbon source with the same reaction set as mentioned above and the gas products were analyzed by gas chromatography-mass spectrometry (JEOL-GCQMS, JMS-K9 and 6890N Network GC system, Agilent Technologies). The apparent quantum efficiency (AQE) at 420 nm was calculated by the following equation: AQE = (2  $\times$  amount of CO molecules evolved in unit time/number of incident photons in unit time)  $\times$  100%.

### 2.4. Computational methods

All calculations were carried out with VASP (Vienna ab initio simulation package) code based on the density functional theory (DFT). The generalized gradient approximation (GGA) was used for the exchange-correlation energy. A plane-wave expansion for the basis set with a cutoff energy of 450 eV was employed. 2  $\times$  2  $\times$  1 Monk-horst k-point meshes was used for the Brillouin-zone integrations of the slab model, respectively. All atoms are relaxed until the residual Hellmann-Feynman force was less than 0.04 eV/Å. Moreover, the convergence for energy is chosen as 10<sup>−5</sup> eV.

## 3. Results and discussion

EDTA is widely used as a chelating agent for transition metal ions like Ni<sup>2+</sup>, Co<sup>2+</sup>, to form hexadentate metal-EDTA complex. We utilize the Co-EDTA decomposition for the chemical anchoring of Co(II) species on the CdS surface through calcination the mixture of CdS and Co-EDTA (with the mole proportion of Co-EDTA to CdS equals to 0.7%) at different temperatures as illustrated in Fig. 1, resulting in the CdS-CoE-*x* (*x* represent the calcination temperature). Decarboxylation of the carboxylate groups in Co-EDTA can be inferred from the decreased absorbance at around 1700, 1400 and 1100 cm<sup>−1</sup> in the *in situ* FTIR spectra, as well as the emerged CO<sub>2</sub> signal at 2350 cm<sup>−1</sup> originated from the gaseous phase. After calcination under 350 °C for 1 h, the resulted CdS-CoE-350 consists a thin layer on the surface of CdS as shown in the HRTEM image, without forming visible nanoparticles (Fig. 1). The uniform dispersion of Co element is confirmed from the energy-dispersive x-ray spectroscopy (EDS) analysis mapping in scanning transmission electron microscope (STEM) (inset of Fig. 1 and Fig. S1). TEM and HRTEM images of the resultant samples from other calcination temperatures such as CdS-CoE-300 and CdS-CoE-400 are shown in Fig. S2, in which, similar thin layer is found in CdS-CoE-300, while small nanoparticles are formed in CdS-CoE-400.

The x-ray diffraction pattern (XRD) (Fig. S3a) also confirmed the maintained pure hexagonal phase of CdS with P6<sub>3</sub>mc space group for all the Co modified CdS. FT-IR absorption spectrum of CdS-CoE-*x* in Fig. S3b exhibit the signals at 1148, 880, 1452 and 1600–1700 cm<sup>−1</sup>, proving the existence of C–N, Co–N, –CH<sub>2</sub>– and COO<sup>−</sup>, with decreased absorbance from COO<sup>−</sup> at elevated temperature. It is inferred that COO<sup>−</sup>, C–N and –CH<sub>2</sub>– groups from EDTA ligands can be reserved under moderate calcination. The UV–vis diffuse reflectance spectra (Fig. 2) show that CdS-CoE-*x* samples have similar absorption edges to pure CdS, although with slightly increased absorption toward visible light caused by the fluctuation of background noise. X-ray photoelectron spectroscopy (XPS) (Fig. S4) confirmed the presence of C, N, O and the similar Co(II) state in CdS-CoE-*x*.

To further verify the microstructure of the Co(II) species on CdS-CoE-350 and the Co(II) structure difference between CdS-CoE-350 and CdS-CoE-300, the X-ray absorption near-edge structure (XANES) spectroscopy and the Co K-edge extended x-ray absorption fine structure (EXAFS) spectrometry were utilized. The overall profile of the Co K-edge XANES spectra of CdS-CoE-300 and CdS-CoE-350 are obviously different from those of metallic Co and CoS (Fig. S5), suggesting a disparate Co location environment. As shown in the EXAFS Fourier

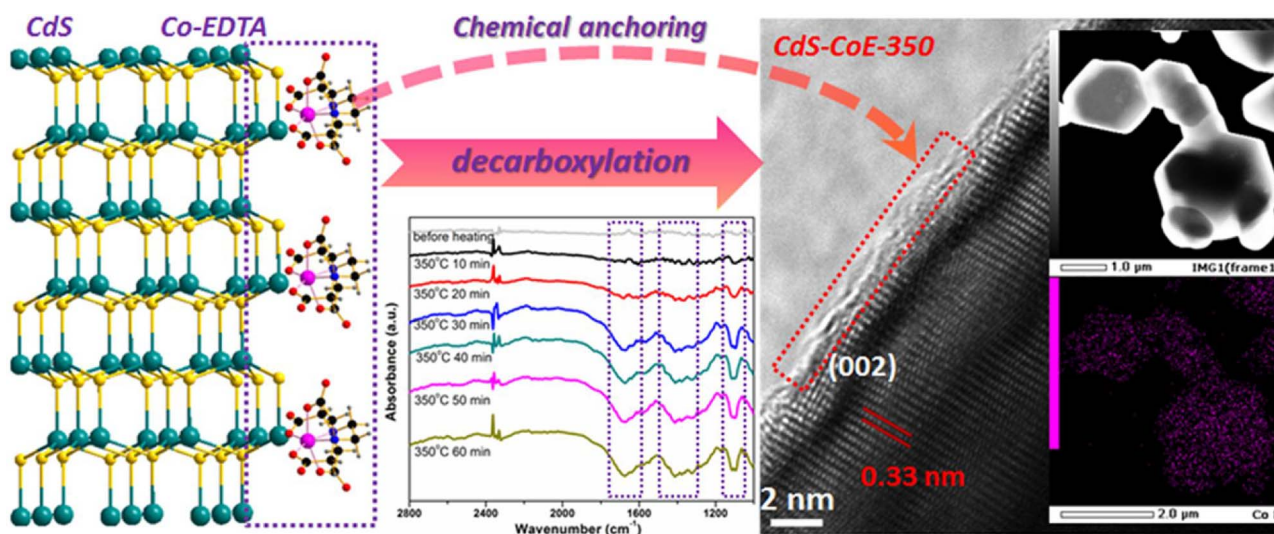


Fig. 1. Schematic illustration for the chemical anchoring of the Co species on the CdS surface through the controlled decomposition of Co-EDTA precursor. Middle: *in situ* FTIR spectra measured during the calcination of Co-EDTA at 350 °C; Right: HRTEM of resulted CdS-CoE-350; inset: STEM image and EDS elemental mapping of CdS-CoE-350.

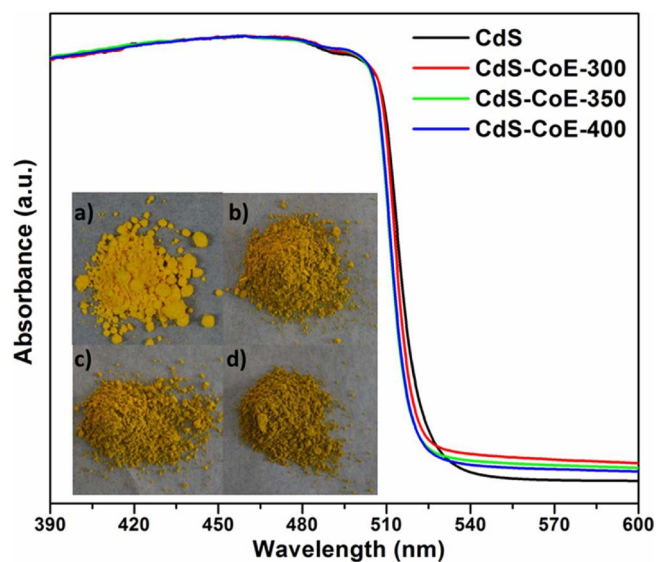


Fig. 2. UV-vis diffuse reflectance spectra of pure CdS, CdS-CoE-x; inset: photograph of CdS (a) and CdS-CoE-x samples (b: CdS-CoE-300; c: CdS-CoE-350; d: CdS-CoE-400).

Transforms (FTs) in Fig. 3a, the scattering peaks in the low R-position range of 1–2.2 Å for CdS-CoE-350 can be fitted as the result of the scattering pairs of Co-N(O) and Co-S [35,36]. As referenced samples, CoS and Co foil exhibit obviously different radial structural functions (RSFs) spectra, which contain the typical Co-S and Co-Co scattering pair in the first shell, respectively. The EXAFS fitting results in Table S1 confirmed that the local Co(II) in CdS-CoE-350 is coordinated with nitrogen(oxygen) and sulfur atoms, with the respective coordination number of surrounding nitrogen(oxygen) and sulfur atoms close to 2, which means Co(II) in CdS-CoE-350 is tetra-coordinated on the CdS surface, although O and N can't be distinguished. While for CdS-CoE-300, the Co K-edge EXAFS Fourier Transform (Fig. S6) shows asymmetrical scattering peaks with R-space from 1.0 to 2.1 Å, which can be assigned well to the scattering shells of Co-O(N), Co-N(O) and Co-S. The EXAFS fitting results indicated that the local Co(II) in CdS-CoE-300 is coordinated with 2-oxygen, 2-nitrogen and 1-sulfur atoms in the distance of 1.45, 1.59 and 1.89 Å, respectively, which means Co(II) in CdS-CoE-300 is penta-coordinated on the CdS surface [37]. In brief, Co(II) could be attached on CdS through coordination with edged sulfur from CdS, forming a penta-coordinated structure and a tetra-coordinated

structure, at 300 °C and 350 °C respectively. In summary of the above, it is concluded that different discrete Co(II) species can be planted on the surface of CdS through bonding with the surface unsaturated sulfur, as a result of the controlled decarboxylation of EDTA ligands, instead of forming the continuous extended structure in nanoparticles. Thermogravimetry analysis (TGA) was used to further track the decomposition of Co-EDTA in the mixture with CdS during the calcination at 300 °C and 350 °C. As indicated in the weight loss curves (Fig. S7), 0.53% of weight loss during the 1 h-calcination at 300 °C indicates an estimated two CO<sub>2</sub> molecules releasing for every Co-EDTA molecule, while 0.99% of weight loss after 1 h-calcination at 350 °C suggested around four CO<sub>2</sub> units releasing for every Co-EDTA molecule. Such stepwise decarboxylation agrees well with the FTIR results (Fig. S3b) mentioned above.

CO<sub>2</sub> reduction activity was evaluated in Na<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>SO<sub>3</sub> solution saturated with atmospheric CO<sub>2</sub> under visible light ( $\lambda > 420$  nm) in a closed gas circulation system [1]. Fig. 4a–b showed the time course of CO/H<sub>2</sub> evolution over pure CdS and CdS-CoE-x. Surprisingly, CdS-CoE-350 showed the highest CO evolution rate of 9.8  $\mu\text{mol h}^{-1}$  (i.e., 392  $\mu\text{mol h}^{-1} g_{\text{catalyst}}^{-1}$ ) and the lowest H<sub>2</sub> evolution rate of 46.1  $\mu\text{mol h}^{-1}$ , with a selectivity of 17.5%, while CdS-CoE-300 exhibited the highest H<sub>2</sub> evolution rate of 917.2  $\mu\text{mol h}^{-1}$  and low CO evolution rate of 0.3  $\mu\text{mol h}^{-1}$  (Fig. 4c). Cycling testing (Fig. 4d) indicated that the CO evolution over CdS-CoE-350 is stable with the TOF (towards the Co sites) of 7.94 h<sup>-1</sup>. Isotope experiment was carried out to validate the source of generated CO by using <sup>13</sup>CO<sub>2</sub> as carbon source resolved in NaOH solution to form Na<sub>2</sub>CO<sub>3</sub>. As shown in Fig. S8, the peak at  $m/z = 29$  indicated that the produced <sup>13</sup>CO indeed originated from <sup>13</sup>CO<sub>2</sub> species in the aqueous solution. A comparison of various cocatalyst for CO<sub>2</sub> reduction suggested that the CO evolution rate of CdS-CoE-350 is 42 times, 13 times and 23 times as high as that of pure CdS, CdS loaded with CoCl<sub>2</sub> as cocatalyst precursor, and CdS loaded Pt, respectively (Fig. 4e). To estimate the real performance of photocatalysts, we investigated the apparent quantum efficiency (AQE) of CdS-CoE-350 for CO evolution at 420 nm, which turned out to be 2.2% as listed in Table S2, also outperforming most photocatalysis systems although still quite low compared with that for the photocatalytic hydrogen evolution [38,39]. More importantly, the selectivity of CO<sub>2</sub> reduction over water reduction on CdS-CoE-350 is far higher than on other kinds of catalyst like CdS-CoE-300, pure CdS, CdS loaded with CoCl<sub>2</sub> as cocatalyst precursor, and CdS loaded Pt as shown in Fig. 4c and e. The effect of loaded Co-EDTA ratio on CdS to the CO<sub>2</sub> reduction on CdS-CoE-350 is also investigated. As shown in Fig. 4f, the hybrid with loaded 0.7% mole proportion of Co-EDTA shows the highest CO

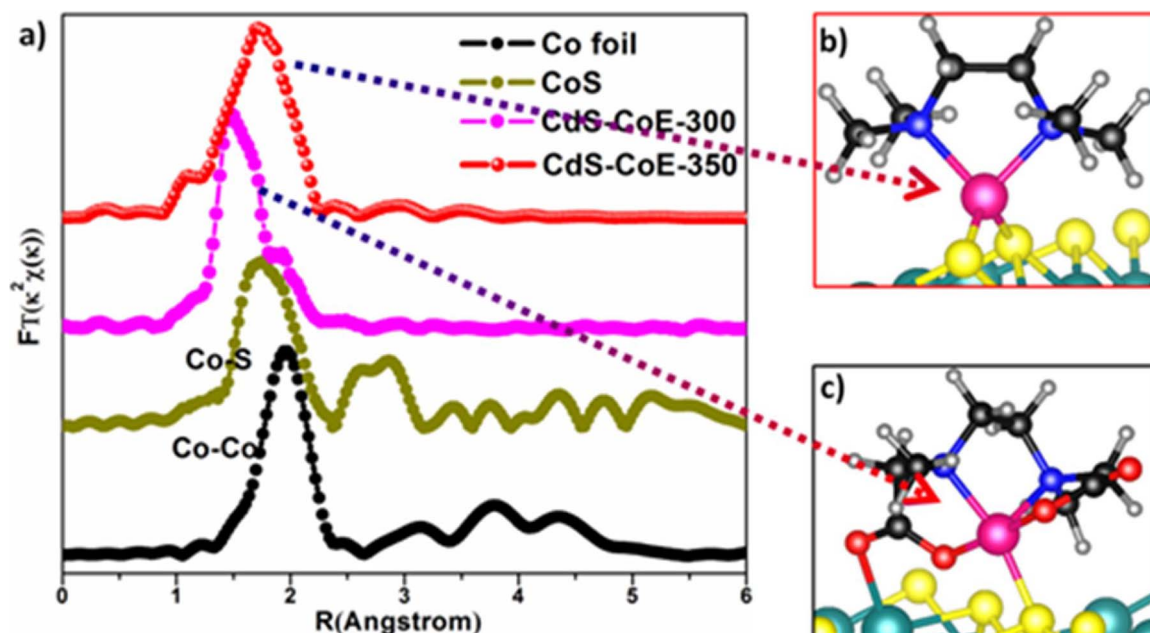


Fig. 3. a) Fourier transform magnitudes of the experimental Co K-edge EXAFS spectra of CdS-CoE and the referenced samples; b and c) the proposed structure of Co species attached on CdS according to the EXAFS fitting results and the DFT modeling.

evolution rate and selectivity, implying that the appropriate amount of Co-EDTA precursor is critical for the dispersion of molecule Co(II) species and the balance between the CO<sub>2</sub> reduction and competitive H<sub>2</sub>O reduction in the resulted CdS-CoE-350. To exclude the possibility of the cocatalysis by the decomposed EDTA, referenced sample prepared by calcination of CdS and EDTA mixture at 350 °C was conducted for the photocatalytic CO<sub>2</sub> reduction. None of CO can be detected after 10 h-irradiation, suggesting that the Co(II) is the catalytic center for CO<sub>2</sub> reduction.

*In situ* electron spin resonance (ESR) measurement was then carried out to unveil the mechanism in the photocatalytic process. To avoid the solvent effect, we collected the ESR signal of IPA-infiltrated CdS-CoE hybrids with and without irradiation under visible light. It shows in Fig.

S9 that in dark condition, CdS-CoE-300 and CdS-CoE-350 showed a broad resonance at  $g = 2.3066$  and  $2.3085$ , respectively, while under irradiation, both of the signals largely weakened. Considering the diamagnetism of Co(I) species, it is reasonable to attribute the weakened signals to the efficient electron trapping by the Co(II) on the surface of CdS-CoE-300 and CdS-CoE-350 [22,40]. We further tried to disclose the original cause for the large gap between the activity of CdS-CoE-300 and CdS-CoE-350. The quenched photoluminescence suggested a decreased electron-hole recombination in CdS-CoE-x than that in pure CdS (Fig. 5) [41]. It is proposed that in CdS-CoE-300 and CdS-CoE-350, the electron-hole recombination is largely prevented due to the efficient electron trapping by the Co(II).

However, there is still no adequate support for the large difference

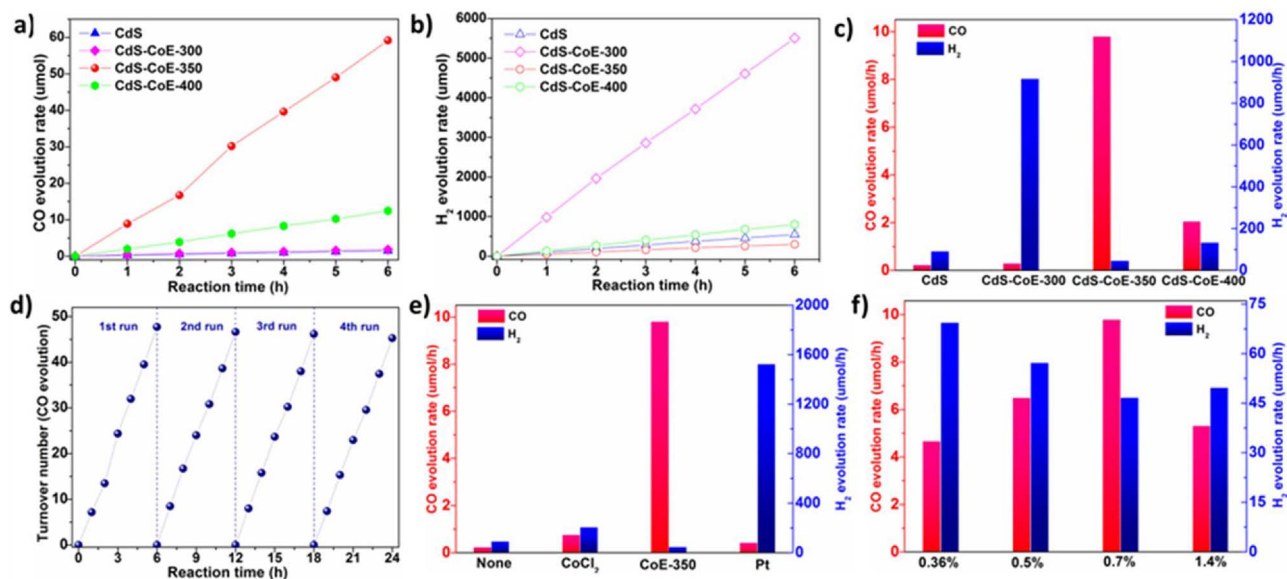


Fig. 4. (a-b) Time-dependent CO and H<sub>2</sub> evolution in the photocatalytic CO<sub>2</sub> reduction with the presence of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>3</sub> over pure CdS, and CdS-CoE-x prepared in different temperatures with 0.7% of initial mole proportion of Co-EDTA to CdS; (c) the comparison of CO and H<sub>2</sub> evolution rate over pure CdS, and CdS-CoE-x (d) Cycling test of CO evolution in the photocatalytic CO<sub>2</sub> reduction over CdS-CoE-350; (e) the comparison of CO and H<sub>2</sub> evolution rate over CdS with different kinds of cocatalyst; (f) CO and H<sub>2</sub> evolution rate over CdS-CoE with various initial mole proportions of Co-EDTA to CdS in the CdS and Co-EDTA mixtures. Light source: 300-W Xe lamp with L42cut-off; Reaction condition: 70 mL of Na<sub>2</sub>CO<sub>3</sub> (0.3 mol/L) and Na<sub>2</sub>SO<sub>3</sub> solution (0.06 mol/L); Catalyst: 25 mg.

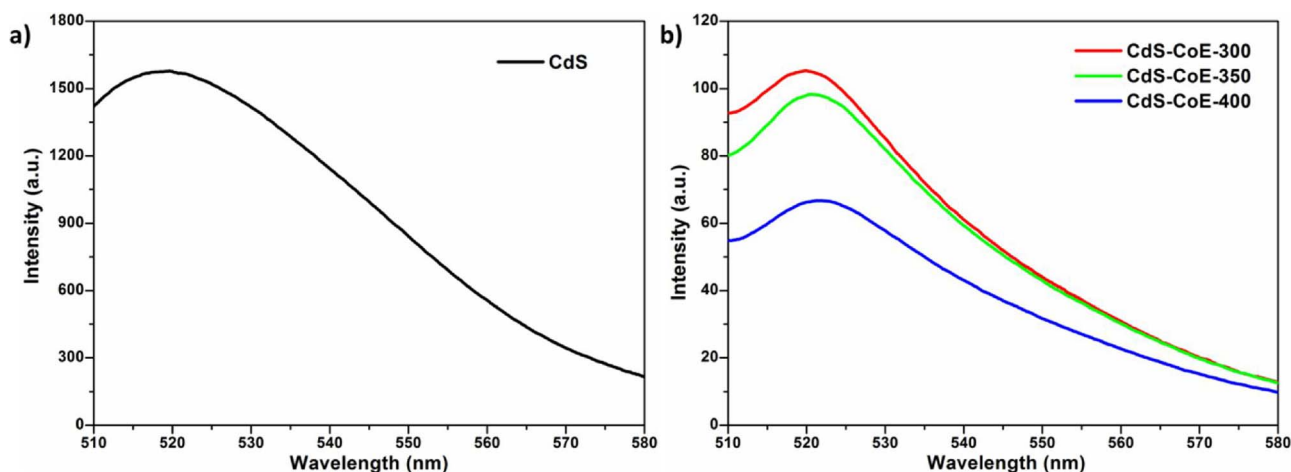


Fig. 5. Photoluminescence spectra of CdS and CdS-CoE-x under 420 nm excitation.

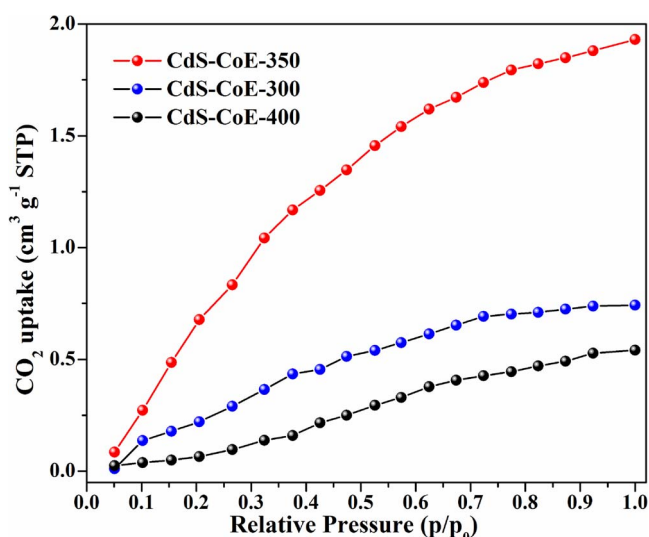


Fig. 6. CO<sub>2</sub> adsorption behaviors for CdS-CoE-300, CdS-CoE-350 and CdS-CoE-400.

of CO<sub>2</sub> reduction selectivity between CdS-CoE-300 and CdS-CoE-350 according to the above analysis. Further investigation is focused on the spatial Co(II) structure in CdS-CoE-300 and CdS-CoE-350. DFT calculation was utilized to monitor the most stable distribution of Co(II) species as shown in Fig. 3b and c. It is speculated that the different Co(II) configurations would exhibit different spatial favor to the attachment of CO<sub>2</sub>. Herein, we used the volumetric CO<sub>2</sub> adsorption measurement to investigate the interaction between carbonate ions and the CdS-CoE-300, CdS-CoE-350 and CdS-CoE-400 surface. As shown in Fig. 6, CdS-CoE-400 showed the lowest affinity and CdS-CoE-300 showed a little higher, while the CdS-CoE-350 exhibited 2.6-fold increased CO<sub>2</sub> adsorption amount compared with CdS-CoE-300. Considering the microstructure characterization results of the Co(II) species on CdS-CoE-350 and CdS-CoE-300 by XANES and EXAFS, it is concluded that the tetra-coordinated structure of Co<sup>2+</sup> shows much higher affinity than the penta-coordinated structure of Co<sup>2+</sup>. We also found out similar high CO<sub>2</sub> affinity in tetra-coordinated Co<sup>2+</sup> in cobalt-porphyrin in our previous work [37], which helps to understand the cause for the best performance of CdS-CoE-350 toward CO<sub>2</sub> reduction. In brief of the above discussion, the efficient and relatively selective CO<sub>2</sub> reduction in aqueous solution can be contributed to well-dispersed Co(II) active sites, the efficient charge transferring, and crucially, the favorable tetra-coordination of Co(II) species in CdS-CoE-350.

#### 4. Conclusions

In conclusion, we have introduced a facial strategy to plant well-dispersed Co(II) species on the CdS surface through the controlled decomposition of Co-EDTA precursors. The resulted CdS-CoE-350, with a tetra-coordinated Co(II) species on the surface, exhibits a selective CO<sub>2</sub> reduction in HCO<sub>3</sub><sup>−</sup> aqueous solution, reaching an efficient photocatalytic CO evolution rate of 9.8 μmol h<sup>−1</sup> (i.e., 392 μmol h<sup>−1</sup> g<sub>(catalyst)</sub><sup>−1</sup>) with a TOF of 7.94 h<sup>−1</sup>. It was found out that the coordinated configuration of cocatalyst plays an important role in the interaction between CO<sub>2</sub> and active sites. The fully utilized Co(II) active sites, special tetra-coordination of Co(II) and the efficient charge transferring contribute to the excellent photocatalytic CO<sub>2</sub> reduction. It is proposed that such kind precursor is promising to construct well dispersed and active transition metal to maximize the catalytic efficiency.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apcatb.2017.12.054>.

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